

# **EXPERIMENTAL STUDIES ON TERNARY DIFFUSIVITIES IN POLYMER SOLUTIONS**

**A Thesis Submitted  
In Partial Fulfilment of the Requirements  
for the Degree of  
MASTER OF TECHNOLOGY**

**By  
DIPANKAR GHOSH**

**to the  
DEPARTMENT OF CHEMICAL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR  
MARCH, 1985**

CHE-1985-M-GHO-EXP

17 JUN 1985

87555

CERTIFICATE

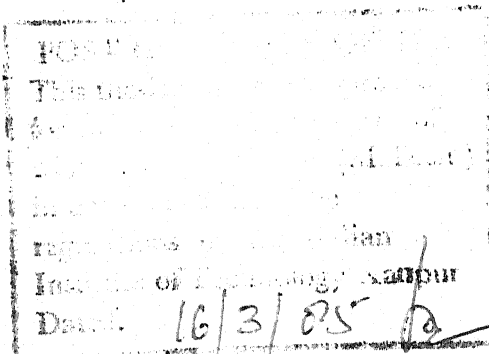
This is to certify that the present work entitled "Experimental Studies on Ternary Diffusivities in Polymer Solutions" by Mr.Dipankar Ghosh has been carried out under our supervision and has not been submitted elsewhere for a degree.

Dr.K.S.Gandhi  
Professor  
Dept. of Chemical Engg.  
Indian Institute of  
Technology  
Kanpur

*Dr.D.P.Rao*

Dr.D.P.Rao  
Assistant Professor  
Dept. of Chemical Engg.  
Indian Institute of  
Technology  
Kanpur

March, 1985



## ACKNOWLEDGEMENTS

I avail myself this opportunity to express my sincere gratitude to Dr.D.P.RAO and Dr.K.S.GANDHI for their valuable guidance in the present work. Special thanks are due to Mr.S.Pandu Ranga Rao for his constant support and valuable suggestions. Finally, I would like to thank all other friends and colleagues, who helped me in numerous ways in course of the work.

*Dipankar Ghosh*

DIPANKAR GHOSH



## CONTENTS

LIST OF TABLES /	i
LIST OF FIGURES /	iii
NOMENCLATURE /	iv
ABSTRACT /	vi
Chapter 1 : INTRODUCTION /	1
Chapter 2 : LITERATURE REVIEW /	5
Chapter 3 : EXPERIMENTAL DETAILS /	18
3.1 Theory of Diaphragm Cell	
3.2 Diaphragm Cell	
3.3 Experimental Procedure	
3.4 Determination of Cell Constant	
3.5 Determination of Composition of Ternary Mixture	
Chapter 4 : RESULTS AND DISCUSSIONS /	31
4.1 Determination of Cell Constant	
4.2 Determination of Binary Diffusivities	
4.3 Determination of Ternary Diffusivities - Analysis of Data	
4.4 Ternary Diffusivities - Results and Discussions	
REFERENCES /	44
APPENDIX-A /	48
APPENDIX-B /	52
APPENDIX-C /	70

LIST OF TABLES

- Table 2.1 : Concentration dependence of binary diffusivity in polystyrene-solvent system / 9
- Table 2.2 : Binary diffusivity of polystyrene-solvent system / 9
- Table 2.3 : Ternary diffusivity of polystyrene-toluene-cyclohexane mixture / 10
- Table 2.4 : Ternary diffusivity of polystyrene 1-polystyrene 2- toluene mixture / 12
- Table 2.5 : Binary diffusivity of polystyrene-cyclohexane mixture - variation with molecular weight of polymer / 14
- Table 3.1 : Parts-list for diaphragm cell / 24
- Table 4.1 : Cell constants determined using toluene-cyclohexane binary mixture at 28°C / 32
- Table 4.2 : Binary diffusivity of benzene-cyclohexane mixture at 28°C / 33
- Table 4.3 : Binary diffusivity of polystyrene-toluene mixture at 28°C / 34
- Table 4.4 : Multicomponent diffusivities of polystyrene-toluene-cyclohexane mixture at 28°C / 39
- Table A.1 : Calibration data for toluene-cyclohexane binary mixtures at 25°C / 48
- Table A.2 : Calibration data for polystyrene-toluene-cyclohexane ternary mixture at 25°C / 49
- Table B.1 : Binary data for toluene-cyclohexane mixture at 25°C / 52
- Table B.2 : Binary data for benzene-cyclohexane mixture at 28°C / 53

- Table B.3 : Binary data for polystyrene-toluene mixture at 28°C / 54
- Table B.4 : Ternary raw data (Set 1) for polystyrene-toluene-cyclohexane mixture at 25°C / 55
- Table B.5 : Ternary raw data (Set 2) for polystyrene-toluene-cyclohexane mixture at 25°C / 56
- Table B.6 : Ternary raw data (Set 3) for polystyrene-toluene-cyclohexane mixture at 25°C / 57
- Table B.7 : Smoothened ternary data (Set 1) for polystyrene-toluene-cyclohexane mixture at 25°C / 58
- Table B.8 : Smoothened ternary data (Set 2) for polystyrene-toluene-cyclohexane mixture at 25°C / 59
- Table B.9 : Smoothened ternary data (Set 3) for polystyrene-toluene-cyclohexane mixture at 25°C / 60
- Table B.10 : Ternary  $\rho_i$  vs.  $t$  data (Set 1) for polystyrene-toluene-cyclohexane mixture at 25°C / 61
- Table B.11 : Ternary  $\rho_i$  vs.  $t$  data (Set 2) for polystyrene-toluene-cyclohexane mixture at 25°C / 62
- Table B.12 : Ternary  $\rho_i$  vs.  $t$  data (Set 3) for polystyrene-toluene-cyclohexane mixture at 25°C / 63

LIST OF FIGURES

- Figure 3.1 : Diaphragm cell diffusion / 19
- Figure 3.2 : Construction of diaphragm cell / 23
- Figure 3.3 : Schematic set-up / 26
- Figure A.1 : Calibration curve for toluene-cyclohexane binary mixture at 25°C / 50
- Figure A.2 : Calibration curve for polystyrene-toluene-cyclohexane ternary mixture at 25°C / 51
- Figure B.1 : Binary data for toluene-cyclohexane mixture at 28°C for diaphragm 1 / 64
- Figure B.2 : Binary data for toluene-cyclohexane mixture at 28°C for diaphragm 2 / 65
- Figure B.3 : Binary data for benzene-cyclohexane mixture at 28°C / 66
- Figure B.4 : Ternary data for polystyrene-toluene-cyclohexane mixture (Set 1) at 28°C / 67
- Figure B.5 : Ternary data for polystyrene-toluene-cyclohexane mixture (Set 2) at 28°C / 68
- Figure B.6 : Ternary data for polystyrene-toluene-cyclohexane mixture (Set 3) at 28°C / 69

NOMENCLATURE

$a_i$	Coefficients in Eqn.3.12
$a_{ij}$	Coefficients in Eqn.3.14
$A$	Total area of pores in diaphragm
$D_o$	Constant in Eqn.2.1 and 2.3
$D_{AB}$	Binary diffusivity
$D_{ij}$	Components of matrix [ D ]
[ D ]	Ternary diffusivity matrix
$(DEB)_D$	Diffusion Deborah number defined in Eqn.2.2
$\bar{j}_A$	Mass flux of component A with respect to mass average velocity in binary mixture
$\bar{j}_i$	Mass flux of component i with respect to mass average velocity in multicomponent mixture
$(\bar{j})$	Mass flux vector with respect to mass average velocity in multicomponent mixture
$k_D$	Coefficient in Eqn.2.1 and 2.3
$l$	Thickness of diaphragm
$M_w$	Weight average molecular weight of polymer
$R_{ij}$	Generalized Stefan-Maxwell coefficients defined in Eqn.1.3
$t$	Run-time of experiment
$t_o$	Time required for development of steady concentration profile in diaphragm
$V_A, V_B$	Volume of compartments of diaphragm cell
$\bar{V}_i$	Partial specific volume of component i in mixture

$x$	Distance in the diaphragm
$\beta$	Cell constant defined in Eqn.3.5 and 3.6
$\theta_D$	Characteristic diffusion time
$\lambda_m$	Characteristic time of fluid
$\sigma_1, \sigma_2$	Eigenvalues of matrix $[D]$
$\rho$	Density of mixture
$\rho_i$	Mass concentration of component $i$ in mixture
$\nabla \rho_i$	Mass concentration gradient of component $i$
$\Delta \rho_i$	Difference in mass concentration of component $i$ between upper and lower compartment of diaphragm cell.

### Subscripts

T	Toluene
CH	Cyclohexane
PS	Polystyrene
U	Upper compartment
L	Lower compartment

ABSTRACT

The diffusivity matrix  $[D]$  in the ternary liquid system comprising ~~of~~ polystyrene, toluene and cyclohexane has been determined employing the diaphragm cell method. The evaluation of the diffusivities from the mass concentration vs. time data was done by a numerical multi-variable optimization technique, namely, the modified Box method. Stronger multicomponent effects as well as concentration dependence of the diffusivities were observed compared to the data reported in the literature for the system with polystyrene of higher molecular weight.

## Chapter 1

### INTRODUCTION

Molecular diffusion arises due to the movement of individual molecules by virtue of their thermal energy. Diffusion phenomenon in gases is described by the kinetic theory. However, the diffusion in liquids and solids are more complex in nature than gases and are not well understood.

The phenomenon of molecular diffusion ultimately leads to a completely uniform concentration of species throughout a mixture, which may initially have been non-uniform. The diffusive mass flux  $\bar{j}_A$  of component A in a binary mixture is given by Fick's first law as:

$$\bar{j}_A = -D_{AB} \nabla \rho_A \quad (1.1)$$

where  $\nabla \rho_A$  is the mass concentration gradient for the species A. Eqn. 1.1 gives the definition of binary diffusivity  $D_{AB}$ .

Multicomponent diffusion is characterised by the fact that the flux of one component is influenced by the concentration gradients of other species except for ideal cases. Fick's first law can be generalised for a multicomponent mixture as

$$(\bar{j}) = -[D](\nabla \rho) \quad (1.2)$$



where, for a mixture containing  $n$  components,  $(\bar{j})$  and  $(\nabla \rho)$  are  $n-1$  dimensional column vectors of the mass flux and mass concentration gradient, respectively and  $[D]$  is an  $n-1$  dimensional square matrix of diffusivities.

The components of the matrix  $[D]$ , i.e., the  $D_{ij}$ 's are termed as multicomponent diffusion coefficients and are different from the binary diffusivity  $D_{AB}$  in Eqn.1.1.

The relation between the fluxes and the mass concentration gradients in a multicomponent mixture is also given by the generalized Stefan-Maxwell equation [Cussler and Lightfoot, 1965a]:

$$\nabla \rho_i = \sum_{\substack{j=1 \\ j \neq i}}^n R_{ij} \bar{V}_j (\rho_i \bar{j}_j - \rho_j \bar{j}_i) \quad (1.3)$$

where, the  $R_{ij}$  are the generalized Stefan-Maxwell coefficients and  $\bar{V}_j$  is the partial specific volume of component  $j$  in mixture.

In a multicomponent system, it is possible to observe various "interaction phenomena" [Toor, 1957; 1964], such as (i) osmotic diffusion (transfer of a component in the absence of composition gradient for that species), (ii) diffusion barrier (no transfer of a component even though a composition gradient exists for it) and (iii) reverse diffusion (diffusion of a species against its

composition gradient). These different interaction phenomena are attributed to what are grossly termed as "multicomponent effects".

Most of the chemical engineering processes, for instance, distillation, absorption, condensation, evaporation etc. involve multicomponent mass transfer; and diffusivity data are required for their analysis and design. Most often one finds that the experimental data are lacking.

Diffusivities of polymer solutions are required for the analysis of many polymer formation and fabrication processes. The rate of polymerisation is strongly influenced by the molecular diffusion of monomers, initiators, long chain free radicals, dead polymer chains or low molecular weight condensation products. The processes such as separation, purification, introduction of plasticisers and other additives, making of foams etc. also involve mass transfer of polymer molecules in different medium and the diffusivity data are required for the analysis of these processes as well. Unfortunately, data in the literature are virtually non-existent for ternary and multicomponent systems involving polymers.

The aim of the present work was to obtain experimental diffusivity data in ternary polymer-solvent system and to examine the multicomponent effects. The Diaphragm cell method [Cussler, 1976] was employed for the measurements.

The system was polystyrene-toluene-cyclohexane, which was chosen for its strong multicomponent behaviour, as reported by Cussler and Lightfoot [1965a] .

## Chapter 2

### LITERATURE REVIEW

In this chapter, a brief discussion is made on the various techniques for experimental determination of binary and ternary diffusivities. This is followed by discussions on the various experimental data reported in the literature and the theories for prediction of diffusivities in polymer-solvent systems.

There are a wide range of methods for measurement of diffusivities in liquids. The use of different types of equipments and these methods have been discussed by Cussler [1976]. More extensive discussion can be found in the book by Dunlop et al [1972]. The mathematical analysis to obtain diffusivities from the raw data are discussed by Crank [1975].

The more frequently used methods employ either the Gouy<sup>u</sup> interferometers or the diaphragm cells of different constructions. The Gouy interferometer [Gosting et al, 1949] measures the refractive index gradient between two interdiffusing solutions with respect to position and time. The diffusion coefficients derived from Gouy interferometric studies are highly accurate, often better than 0.1% [Cussler, 1976]. Most of the studies on polymer-solvent systems, reported in literature, have been done with the Gouy interferometers.

In the diaphragm cell method, the variation of concentration of two interdiffusing solutions separated by a porous diaphragm in the cell is measured with time. These data are utilized to determine the diffusivities as will be discussed in the <sup>following</sup> ~~next~~ chapters.

The effective diameter of the pores in the diaphragm must be such that gross streaming through the diaphragm is avoided, but, at the same time, the pores must be large in comparison with molecular dimensions so that the diffusion will take place under conditions comparable with those obtained in free diffusion. Diaphragms made of 2-3 mm thick fritted glass had been used to determine diffusivity of KCl in aqueous solution [Gordon, 1945]. However, thin diaphragms made of different synthetic materials are used now-a-days, which are more suitable for using with organic solvents and polymers. The design of diffusion cells, since its earliest uses in the forties, has also been modified according to requirements. A later version of a diaphragm cell has been described by Robinson and Stokes [1959] and a more recent version was used by Geankoplis et al [1978] to measure diffusivity of urea and KCl in albumin solution.

A comparison of the Gouy interferometer and the diaphragm cell [Cussler and Dunlop, 1966] asserts that no theoretical advantage in either of them should be expected. The mathematics involved in both the cases has got similar

degree of difficulty. The principal advantage of the diaphragm cell is its simplicity of construction and use. Therefore, even though the ~~Gouy~~<sup>u</sup> interferometer is often more accurate, the diaphragm cells are used when ease of obtaining data is one of the concerns.

There are two techniques for the analysis of raw ternary data to determine diffusion coefficients [Cussler, 1976]. One is the pseudo-binary method [Fujita and Gosting, 1960; Revzin, 1972], used commonly with the ~~Gouy~~<sup>u</sup> interferometers.

The other technique based on numerical minimization of a suitably formulated objective function, is discussed in detail in Chapter 4. A numerical technique, based on the non-linear least-squares is described by Patel et al. [1969].

Experimental data for polymer-solvent systems are extremely meagre. One of the earliest experimental work was reported by Tsvetkov and Klenin [1958], who studied the diffusion of two grades of polystyrene ( $M_w = 3,500,000$  and  $5,000,000$ ) in different solvents such as butanone and carbontetrachloride. The differential diffusion coefficients were determined by keeping the concentration difference as small as  $10^{-4}$  g/ml in polarisation interferometer.

. The concentration dependence of diffusivity, described as

$$D = D_0 (1 + k_D c) \quad (2.1)$$

where  $p$  is the concentration of polystyrene in g/ml and  $D_0$  and  $k_D$  are constants, was also studied. The findings are reported in Table 2.1.

Cussler and Lightfoot [1965a] reported binary as well as ternary diffusivity data for polystyrene ( $M_w = 193,000$ ) in toluene and cyclohexane. Measurements were done by a Gomy interferometer at a temperature of  $28.00^\circ\text{C}$ . Actual diffusivity values for different compositions were found by repeating all experiments at the same average concentration but different concentration differences and extrapolating the results to zero concentration difference. Both the binary and the ternary diffusivities showed strong concentration dependence. The ternary coefficients showed large deviations from Fick's law. The cross term coefficients ( $D_{12}$  and  $D_{21}$ ) were found to be much larger than the main term coefficient ( $D_{11}$  and  $D_{22}$ ), as may be seen from the data reported in Table 2.2 and Table 2.3.

Ternary diffusion of mixtures of two monodisperse polystyrene of different molecular weights ( $M_w = 193,000$  and  $M_w = 234,000$ ) in toluene was studied by Cussler and Lightfoot [1965b]. The results also showed large multi-component effects. The results were in qualitative agreement with those values predicted from the extensions of hydrodynamic models [Groot and Mazur, 1962; Scott, 1949; Flory and Krigbaum, 1950]. The results of the experiments are reported in Table 2.4.

Table 2.1 : Concentration dependence of binary diffusivity in polystyrene-solvent system [Tsvetkov and Klemen, 1958]

Note:  $D_0$  and  $k_D$  refer to Eqn.2.1

Mol.wt., $M_w$	Solvent	$D_0$ ( $\text{cm}^2/\text{sec.}$ )	$k_D$ ( $\text{cm}^3/\text{g}$ )
$3.5 \times 10^6$	Butanone	$1.1 \times 10^{-7}$	$1.6 \times 10^2$
$3.5 \times 10^6$	$\text{CCl}_4$	$0.45 \times 10^{-7}$	$1.5 \times 10^2$
$5.0 \times 10^6$	$\text{CCl}_4$	$0.33 \times 10^{-7}$	$6.0 \times 10^2$

Table 2.2 : Binary diffusion coefficient of polystyrene-solvent system [Cussler and Lightfoot, 1965a]

Mol.wt., $M_w$	Mass fraction polymer	Solvent	Diffusivity, $D_{AB}$ ( $\text{cm}^2/\text{sec}$ )
193,000	0.05	Toluene	$8.752 \times 10^{-7}$
		Cyclohexane	$1.010 \times 10^{-7}$



Table 2.3 : Ternary diffusivity of polystyrene-toluene-cyclohexane mixture  
[Cussler and Lightfoot, 1965a]

Set 1

Components : 1 = Polystyrene ( $M_w = 193,000$ )

2 = Cyclohexane

3 = Toluene

Ternary mixture	1	2
$w_1$ $q$	0.0500	0.0500
$w_2$	0.0500	0.9000
$w_3$	$\overset{9000}{0.0900}$	0.0500
$D_{11} \times 10^7$ (cm <sup>2</sup> /sec)	8.9	10.0
$D_{12} \times 10^7$ (cm <sup>2</sup> /sec)	-1.6	1.3
$D_{21} \times 10^7$ (cm <sup>2</sup> /sec)	-8.9	169.6
$D_{22} \times 10^7$ (cm <sup>2</sup> /sec)	203.1	202.0

Continued....

Table 2.3 (Continued):Set 2Components : 1 = Polystyrene ( $M_w = 193,000$ )

2 = Toluene

3 = Cyclohexane

Ternary mixture	1	2
$w_1$	0.0500	0.0500
$w_2$	0.4751	0.0503
$w_3$	0.4749	0.8997
$D_{11} \times 10^7$ (cm <sup>2</sup> /sec)	5.8	1.8
$D_{12} \times 10^7$ (cm <sup>2</sup> /sec)	-6.7	-6.7
$D_{21} \times 10^7$ (cm <sup>2</sup> /sec)	14.5	-0.9
$D_{22} \times 10^7$ (cm <sup>2</sup> /sec)	171.8	178.9

Table 2.4 : Ternary diffusivity of polystyrene 1-  
polystyrene 2-toluene mixture  
[Cussler and Lightfoot, 1965b]

Components : 1 = Polystyrene ( $M_w = 193,000$ )

2 = Polystyrene ( $M_w = 234,000$ )

3 = Toluene

	$w_1 + w_2$	$D_{11} \times 10^7$ ( $\text{cm}^2/\text{sec}$ )	$D_{12} \times 10^7$ ( $\text{cm}^2/\text{sec}$ )	$D_{21} \times 10^7$ ( $\text{cm}^2/\text{sec}$ )	$D_{22} \times 10^7$ ( $\text{cm}^2/\text{sec}$ )
Experi- mental	0.0000	3.77	0.00	0.00	3.45
	0.0250	4.46	1.14	1.73	4.69
	0.0500	4.20	4.17	4.21	4.23
Theore- tical	0.0000	3.77	0.00	0.00	3.45
	0.0250	4.43	2.94	2.72	4.32
	0.0500	5.10	5.92	5.47	5.32

Binary diffusivity data for polystyrene in cyclohexane from the Gouy interferometric studies were reported by Cowie and Cussler [1967], which showed variation of diffusivity with molecular weight of polystyrene. The measured diffusivities were actually those averaged over the polydispersity of the polymer, which was, however, very low. Results are reported in Table 2.5.

Diffusion of polystyrene in cyclohexane at the dilute and the infinitely dilute range were studied by Vrentas and Duda [1976a,b]. Diffusivity data taken from various sources were examined against those predicted on the basis of the Kirkwood-Riseman theory [Kirkwood and Riseman, 1948; Yamakawa, 1971]. The predictions and the experimental data were found to be in good agreement for polystyrene-cyclohexane system.

Diffusion of ethylbenzene in molten polystyrene ( $M_w = 275,000$ ) was studied systematically by Duda and Ni [1978] at the temperature range from 115.5 to 178°C and for concentrations as high as 70 weight percent ethylbenzene. Experiments were carried out using a quartz-spring sorption apparatus [Duda et al, 1973], which was modified for high temperature measurements. The data show strong concentration dependence of diffusivity, which is more pronounced at low temperatures and lower solvent concentrations. From the comparison of these data with those predicted from the free volume theory [Duda and Vrentas 1977a,b],

Table 2.5 : Binary diffusivity of polystyrene-cyclohexane mixture - variation with molecular weight of polymer  
[Cussler and Cowie, 1967]

Temp. (°C)	Molecular weight	Diffusivity, $D_{AB} \times 10^7$ (cm <sup>2</sup> /sec)
35	194000	3.082
	414000	2.225
	929000	1.436
25	181000	3.494
	481000	1.816
	1040000	1.157

it is found that the theory consistently overestimated the diffusivities.

The mass transfer in the concentrated polymer solutions can not be described by the classical theories of diffusion. This non-classical behaviour is supposed to be associated with the sluggish relaxation of the large polymer molecules from the bulk. These behaviours were studied by Alfrey [1965] . Work was later extended by Hopfenberg and Frisch [1969] and Duda [1975]. A diffusion Deborah number was introduced as

$$(\text{DEB})_D = \frac{\lambda_m}{\theta_D} \quad (2.2)$$

where  $\lambda_m$  is the characteristic time of the fluid and  $\theta_D$  is the characteristic diffusion time. The value of Deborah number for a given set of conditions identifies the type of diffusional transport that can be expected. When Deborah number is small (say less than 0.1), the local relaxation in the system is fast compared to the diffusion process. On the other hand, a large Deborah number (say greater than 10) signifies that there is essentially no time variation of the structure of the polymer during diffusion process. This type of diffusional transport was denoted as elastic diffusion [Vrentas and Duda, 1979] .

The characteristics of polymer solutions change significantly with the change in concentration. In the

infinitely dilute polymer solution, the polymer molecules are widely dispersed and there are no interactions between the individual polymer chains. As the polymer concentration is increased, the polymer molecules begin to interact hydrodynamically with each other, even though the domains of the individual polymer molecules do not yet overlap. This concentration region is referred to as the dilute solution region. At a further increased polymer concentration, the domains of the polymer molecules begin to overlap so that there is a considerable amount of polymer-polymer contact, and entanglements are formed between polymer molecules. This concentration region is denoted as concentrated polymer solution [Vrentas and Duda, 1979].

Although a general theory which can describe molecular diffusion throughout the complete concentration range is yet to be developed, independent theories have been proposed which are applicable to specific region of the concentration intervals. A brief discussion is given below.

For dilute polymer solutions, the concentration dependence of mutual diffusion coefficients can be expressed as [Vrentas and Duda, 1979 ]:

$$D = D_0 (1 + k_D \rho_2) \quad (2.3)$$

where  $\rho_2$  is the mass concentration of the polymer in the solution,  $D_0$  is the mutual diffusion coefficient at zero polymer concentration and  $k_D$  is a coefficient. Thus, in dilute polymer solutions, prediction of diffusivity reduces to determination of  $D_0$  and  $k_D$  at a particular set of conditions for the particular system. The determination of  $D_0$  involves consideration of intramolecular forces, whereas both intra- and intermolecular forces are to be considered in the determination of  $k_D$ . Various methods for these along with references are discussed by Duda and Vrentas [1979].

Molecular diffusion in concentrated polymer solution is a more complex phenomenon and is not well understood. Nevertheless, the free volume theory described by Fujita [1968], which was further modified by Vrentas and Duda [1977a,b], rendered positive contribution in understanding the phenomena and also in prediction of diffusion coefficients.

The predictive methods described in the preceding section are based on approximate theories of molecular diffusion. To evaluate these methods and to implement necessary improvements, reliable diffusivity data are required. However, very little experimental work has been done to determine diffusivities in polymer-solvent systems, most of which is due to Cussler and Lightfoot [1965a,b]. Various notable experimental works on determination of diffusivities are listed by Cussler [1976].



## Chapter 3

### EXPERIMENTAL DETAILS

#### 3.1 Theory of Diaphragm Cell

The diaphragm cell used for the determination of diffusivity is shown schematically in Figure 3.1. It consists of two compartments A and B, with provisions for stirring, separated by a diaphragm, which can either be a porous plug or a membrane [Stokes, 1950, 1951]. The compartments are filled with solutions of different concentrations and are kept well-stirred. These concentrations change gradually with time as a result of diffusion across the diaphragm. The change in concentration is measured at different intervals of time and the data <sup>are</sup> ~~is~~ used to compute the diffusion coefficient(s) as described below.

For a binary solution, the mass balance equation for the solute within the porous plug or membrane is [Cussler, 1976]

$$\frac{\partial \rho_1}{\partial t} = - \frac{\partial \bar{J}_1}{\partial x} = D_{AB} \frac{\partial^2 \rho_1}{\partial x^2} \quad (3.1)$$

and the boundary conditions are

$$x = 0, \quad \rho_1 = \rho_{1A} \quad (3.2)$$

$$x = l, \quad \rho_1 = \rho_{1B} \quad (3.3)$$

where  $l$  is the thickness of the diaphragm and  $\rho_{1A}$  and  $\rho_{1B}$  are the mass concentrations of component 1 in compartments

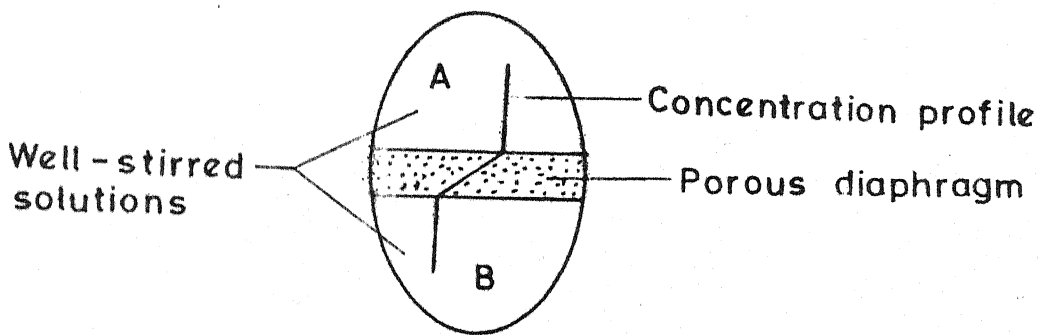


FIG.3.1 DIAPHRAGM CELL DIFFUSION

A and B.

When the volume of the pores in the diaphragm is much less than the volume of the entire diaphragm cell, a steady-state concentration gradient is very quickly established in the diaphragm. However, this is actually a "pseudo-steady state" value, which does change very slowly with time [Cussler, 1976]. With this pseudo-steady state approximation, Eqn.3.1 becomes

$$0 = - \frac{d \bar{j}_1}{dx} = D_{AB} \frac{d^2 \rho_1}{dx^2} \quad (3.4)$$

Integration of this equation and substitution in the overall mass balance equation yields

$$\frac{\rho_{1B} - \rho_{1A}}{\rho_{1B}^o - \rho_{1A}^o} = \exp(-\beta D_{AB} t) \quad (3.5)$$

where the subscript 'o' indicates the initial concentration and  $\beta$  is the cell constant. It is related to the cell parameters as

$$\beta = \frac{A}{I} \left( \frac{1}{V_B} + \frac{1}{V_A} \right) \quad (3.6)$$

where A is the total area of the pores in the diaphragm and  $V_A$  and  $V_B$  are the volumes of the two compartments of the cell.

For binary mixtures with known diffusion coefficient, Eqn.3.5 may be employed to determine the cell constant.

Once the cell constant is known, the same equation can be employed to determine diffusivity of unknown mixtures.

The pseudo-steady state assumption has been thoroughly tested by Mills et al [1968] and it was reported that the above approximation leads to an error less than 3 percent, even when the pore volume is 10 percent of the total volume. Since the pore volume is commonly less than even 1 percent of the cell volume, the approximation is indeed very good. Also, the time required for attainment of the pseudo-steady state within the diaphragm,  $t_o$  was given by [Gordon, 1945]

$$t_o = 1.2 \frac{l^2}{D_{AB}} \quad (3.7)$$

It should be ensured that the experimental run-time  $t$  is such that  $t \gg t_o$ .

The extension of the binary diffusion equations for the diaphragm cell for the ternary diffusion yields the following equations [Toor, 1964a,b; Cussler, 1976]:

$$\begin{aligned} \Delta \rho_1 = & \frac{(D_{11} - \sigma_2) \Delta \rho_1^0 + D_{12} \Delta \rho_2^0}{\sigma_1 - \sigma_2} \exp(-\beta \sigma_1 t) \\ & + \frac{(D_{11} - \sigma_1) \Delta \rho_1^0 + D_{12} \Delta \rho_2^0}{\sigma_2 - \sigma_1} \exp(-\beta \sigma_2 t) \end{aligned} \quad (3.8)$$

$$\Delta \rho_2 = \frac{D_{21} \Delta \rho_1^0 + (D_{22} - \sigma_2) \Delta \rho_2^0}{1 - 2} \exp(-\beta \sigma_1 t) + \frac{D_{21} \Delta \rho_1^0 + (D_{22} - \sigma_1) \Delta \rho_2^0}{\sigma_2 - \sigma_1} \exp(-\beta \sigma_2 t) \quad (3.9)$$

where,

$$\sigma_1 = \frac{1}{2} (D_{11} + D_{22} + \sqrt{(D_{11} - D_{22})^2 + 4 D_{12} D_{21}}), \quad (3.10)$$

$$\sigma_2 = \frac{1}{2} (D_{11} + D_{22} - \sqrt{(D_{11} - D_{22})^2 + 4 D_{12} D_{21}}) \quad (3.11)$$

the symbol  $\Delta$  represents the difference between the upper and the lower compartments and the  $D_{ij}$ 's are the ternary diffusion coefficients. They can be evaluated from  $\rho_i$  vs.  $t$  data. Since there are four unknowns (the  $D_{ij}$ 's) and only two equations, it is necessary to perform at least two experiments to determine the four  $D_{ij}$ 's. However, according to Cussler [1976], twice the minimum number of experiments is desirable to obtain accurate values of diffusivities.

### 3.2 Diaphragm Cell

The diaphragm cell used in the present work was similar to the one described by Geankoplis et al [1978]. A scale drawing of the cell is given in Figure 3.2.

The cylindrical shell and the caps of the cell were made of nylon, as nylon is unaffected by the organic solvents used.

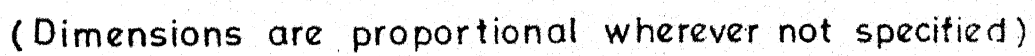


Table 3.1 : Parts-list for diaphragm cell  
[Ref. : Fig.3.2]

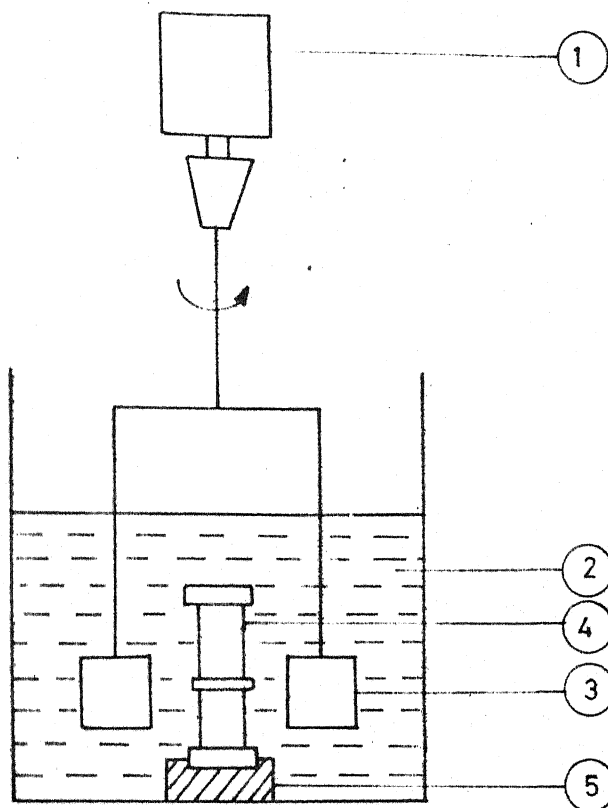
Part	Description
1	4 mm nylon screw used as cap
2	Magnetic stirrer
3	Brass fastener
4	Steel capillary with 0.5 mm bore
5	Teflon gasket
6	Nylon shell
7	Teflon diaphragm with 0.5 $\mu$ m pores
8	Steel plates with 19x4 mm holes
9	Nylon column to support magnet
10	<i>Nylon disc</i>

The diaphragm used was made of teflon and was obtained from M/S. Millipore Corporation, USA. According to the manufacturer's specification, it had straight pores of  $0.5 \mu m$  size. The diaphragm was housed between two stainless steel plates with coinciding large holes so that a large portion of the diaphragm was exposed to the solutions both the sides. Two cylindrical teflon-coated magnetic stirrers were placed in the two compartments of the cell. A nylon column was provided in the lower compartment to support the magnet near the diaphragm and a similar column was provided in the upper compartment to maintain geometric similarity. The magnetic stirrers were operated by rotating two powerful horse-shoe magnets suspended from a frame outside the cell. Screw-threaded nylon caps were used to plug the holes in the compartments, those were used for transfer of solutions in and out of the cell. A narrow stainless steel capillary tube was provided in the upper compartment to allow overflow of the excess liquid while the hole is being plugged. A drawing of the set-up is given in Figure 3.3.

### 3.3 Experimental Procedure

The two compartments of the cell were filled with two solutions of different composition as follows. The denser among the two was introduced in the bottom compartment to prevent mixing due to gravity.





1. Stirrer motor.    2. Temp. controlled water bath.  
3. Horse-shoe magnets.    4. Diaphragm cell.  
5. Base, to which the cell is fastened.

FIG.3.3 SCHEMATIC SET-UP

First, the cell was inverted and the denser solution was introduced into the bottom compartment (which was actually at the top then) with a syringe. After filling, as the nylon stopper was tightened, the excess solution was passed through the porous diaphragm to the other compartment. The absence of air bubble was checked by visual observation against strong light. The cell wall was actually translucent and air bubbles were visible if they were present.

Now the other compartment was rinsed quickly and then filled with the lighter solution. After filling, the nylon stopper was inserted and as it was tightened, the excess solution overflowed through the capillary tube provided for this purpose. Immediately after the capillary tube was covered with a teflon cap.

Then the cell was placed in a constant temperature water bath maintained at  $28 \pm 0.5^{\circ}\text{C}$  and stirring was started. It was found that the magnetic stirrers inside failed to rotate at high rpm. The stirrer was operated at 80 rpm for all the runs. After a predetermined time, the cell was taken out of the bath, the solutions from the two compartments were transferred to sample bottles using a syringe, and were subjected to subsequent analysis to determine their composition. This is described in the following sections.

### 3.4 Determination of Cell Constant

Eqn.3.5 was employed to determine the cell constant using binary mixtures of toluene and cyclohexane, the diffusivity of which was reported by Cussler and Lightfoot [1965a].

A calibration curve of mass fraction of toluene ( $w_T$ ) vs. density ( $\rho$ ) of toluene-cyclohexane binary mixture at 25°C was found. The densities were measured with a 20 ml specific gravity bottle using a Mettler H20 balance, which can weight with accuracy upto 5 decimal places of a gram. The calibration and the curve are given in Appendix A.

The calibration curve was fitted to the polynomial

$$w_T = a_1 + a_2 \rho + a_3 \rho^2 + a_4 \rho^3 \quad (3.12)$$

The coefficients were determined by non-linear least-square technique and are given below:

$$\begin{aligned} a_1 &= -1.8681 \\ a_2 &= 6.2674 \\ a_3 &= -7.0672 \\ a_4 &= 2.6948 \end{aligned} \quad (3.13)$$

The initial and the final mass fractions of components in the solution were determined using Eqn.3.12 from the

density measurements. Mass concentrations were consequently determined. The cell constant was calculated from three runs with toluene-cyclohexane mixture and the average value was used for the evaluation of ternary diffusivities. The determination of cell constant was done every time the diaphragm was changed.

### 3.5 Determination of Composition of Ternary Mixtures

It is possible to determine the diffusivities of a ternary mixture from the measurement of initial and final densities of the mixtures. But this method requires 4 sets of experimental data to obtain the diffusivities [Cussler and Dunlop, 1966]. However, if the mass concentrations of the initial and final solutions are known, then only 2 sets of data are required. Hence, in the present work, mass concentrations of the individual species were determined with the help of calibration as described below.

Densities were measured for known composition of polystyrene-toluene-cyclohexane mixtures and a three-parameter calibration curve was made. The data and the curve are given in Appendix A. The mass fraction of toluene  $w_T$  in the ternary mixture was fitted to the polynomial

$$w_T = \sum_{i=0}^3 \sum_{j=0}^3 a_{ij} w_{PS}^i \rho^j \quad (3.14)$$

where  $w_{PS}$  is the polystyrene mass fraction and  $\rho$  is the mixture density at 25°C. The NAG subroutine E02DAF, which employs the non-linear least-square technique, was employed to obtain the coefficients and are given below:

$$\begin{array}{llll} a_{11}=1.1115 & a_{21}=-3.8026 & a_{31}=-18.9424 & a_{41}=-23.9294 \\ a_{12}=58.3285 & a_{22}=41.1453 & a_{32}=45.5083 & a_{42}=34.2428 \\ a_{13}=78.2732 & a_{23}=79.6377 & a_{33}=67.7887 & a_{43}=62.0261 \\ a_{14}=114.1580 & a_{24}=105.4090 & a_{34}=98.7856 & a_{44}=93.4207 \end{array}$$

(3.15)

To analyse unknown samples, the density of the sample was measured first. Then a known amount of mixture (15 ml) was allowed to dry on a petri dish in an oven maintained at 90°C. When all the volatile solvents were removed (this was confirmed from the constancy in weight at repeated weighing), the weight of the polymer residue was determined. From this, the mass fraction of the polymer was directly obtained. From the knowledge of  $\rho$  and  $w_{PS}$ ,  $w_T$  was determined using Eqn.3.14 and the mass fraction of cyclohexane,  $w_{CH}$ , was also determined. Mass concentrations of all the components were subsequently calculated.

The data as well as the calibration curve is given in Appendix A. The determination of diffusivity matrix  $[D]$  from those data is discussed in the next chapter.

## Chapter 4

### RESULTS AND DISCUSSION

In this chapter the determination of cell constant, verification of the reliability of the diaphragm cell and the ternary diffusivities are presented.

#### 4.1 Determination of Cell Constant

Two diaphragms were employed in the present study, and the cell constants with these diaphragms were determined using a test solution of toluene and cyclohexane. The mixture density ( $\rho$ ) and mass concentration of toluene ( $\rho_T$ ) vs. run-time data are reported in Appendix B and the results are summarized in Table 4.1.

From Table 4.1, it can be seen that the cell constants obtained were nearly the same with different durations of run (run-time) and also for the two diaphragms.

#### 4.2 Determination of Binary Diffusivities

Binary diffusivity of benzene-cyclohexane and polystyrene-toluene system were determined and the values were compared with the values reported in the literature to check the reliability of the present method. The density/mass concentration vs. run-time data are reported in Appendix B and the results are summarized in Tables 4.2 and 4.3.

Table 4.1 : Cell constants determined using toluene-cyclohexane binary mixture at 28°C

Average Composition :  $w_T = 0.5403$

$w_{CH} = 0.4597$

Diffusivity  $D_{AB} = 1.944 \times 10^{-5} \text{ cm}^2/\text{sec.}$

[Cussler and  
Lightfoot, 1965a]

	Run-time (hr)	Cell constant ( $\text{cm}^{-2}$ )	Average cell constant ( $\text{cm}^{-2}$ )
Diaphragm 1	0.5	12.19	
	1.0	12.50	12.35
	1.5	12.36	
Diaphragm 2	0.5	12.70	
	1.0	12.12	12.39
	1.5	12.35	

Table-4.2 : Binary diffusivity of benzene-cyclohexane mixture at 28°C

Average composition :  $w_B = 0.7875$

$w_{CH} = 0.2125$

i.e., 20 mol % cyclohexane

Cell constant =  $12.35 \text{ cm}^{-2}$

Run-time (hr)	Diffusivity, $D_{AB}$ ( $\text{cm}^2/\text{sec.}$ )	Average $D_{AB}$ ( $\text{cm}^2/\text{sec.}$ )	Reported $D_{AB}$ at 25°C [Mills, 1965] ( $\text{cm}^2/\text{sec.}$ )
0.5	$1.944 \times 10^{-5}$		
1.0	$2.185 \times 10^{-5}$	$2.03 \times 10^{-5}$	$1.90 \times 10^{-5}$
1.5	$1.956 \times 10^{-5}$		



Table 4.3 : Binary diffusivity of polystyrene-toluene mixture at 28°C

Average composition :  $w_{PS} = 0.05$

$w_T = 0.95$

Cell constant =  $12.35 \text{ cm}^{-2}$

Molecular weight, $M_w$	Diffusivity, $D_{AB}$ ( $\text{cm}^2/\text{sec.}$ )
32,000	$1.039 \times 10^{-6}$

The diffusivity value for benzene-cyclohexane system can be seen to be in good agreement with the value reported by Mills [1965] and the small difference may be attributed to the difference in temperatures ( $3^{\circ}\text{C}$ ) at which they were determined.

The diffusivity for polystyrene-toluene mixture was found for polystyrene having a weight average molecular weight ( $M_w$ ) 32,000. It is known that the diffusivity depends on the molecular weight of polymer. Data for the polymer of this particular molecular weight was not available for comparison. However, Vrentas and Duda [1979] gave the dependence of diffusivity for polystyrene and ethylbenzene mixture, for the polymer having molecular weight ranging from  $1 \times 10^5$  to  $10 \times 10^5$ . Extrapolation of this data to the polymer molecular weight 32,000 gave a value  $1 \times 10^{-6} \text{ cm}^2/\text{sec}$ , which is in close agreement with the one obtained in this work. Since nature of toluene as solvent is close to ethylbenzene, the diffusivities are not expected to be too much different. Moreover, Cussler and Lightfoot [1965a] reported a value of diffusivity  $8.752 \times 10^{-7}$  for polystyrene-toluene mixture of same composition for a polymer of molecular weight 193000. The diffusivity is approximately 85 percent of the value obtained in this work. This is again agreeable considering the large difference in the molecular weight.

Thus the cell and the method employed were considered satisfactory for the determination of diffusivities of binary and ternary mixtures.

#### 4.3 Determination of Ternary Diffusivities-Analysis of Data

To determine ternary diffusivities, experiments were performed with polystyrene-toluene-cyclohexane mixtures at three different compositions. For each of these compositions, 4 to 5 independent experiments were performed with different run-times. The run-times were chosen such that there was a significant composition difference between the initial and the final values. For the sake of convenience, initial concentration differences ( $\rho_i^0 = \rho_{iA}^0 - \rho_{iB}^0$ ) between the upper and lower compartments were not varied from experiment to experiment, although this was not required. The samples were collected after each run and were analysed for their mass concentrations as described earlier [Section 3.5].

To determine the components of the diffusivity matrix from  $\rho_i$  vs  $t$  data, the following objective function was chosen:

$$R = \sum_{j=1}^n \sum_{i=1}^2 [\Delta \rho_i (\text{expt}) - \Delta \rho_i (\text{calc})]^2_j \quad (4.1)$$

where  $\Delta \rho_i$  (expt) are the differences in the mass concentrations of component  $i$  between the upper and the lower

compartments of the cell at time  $t$ ,  $\Delta \rho_i$  (calc) are those calculated using Eqn.3.8 and 3.9 with a guess matrix  $[D]$  and  $n$  is the number of experiments.

The objective function was subjected to minimisation to obtain the matrix  $[D]$ . The minimization was carried out using a subroutine (CPX) developed by Hughes and Malik [1979] . It utilised a multivariable search technique introduced by Box [Beveridge and Schechter, 1970] . Domains of the  $D_{ij}$ 's were supplied in the form of upper and lower limits. The program chose 7 different combinations of  $D_{ij}$  values at random within these domains. The worst combination (for which the objective function is the largest) was replaced by a new combination selected by a specific criteria. The process continued till the minima for the objective function was determined with the desired accuracy, which can be set by multiplying the objective function by a suitable large number. The program which utilises the subroutine (CPX) is listed in Appendix C.

The proper choice of the upper and the lower limits of the  $D_{ij}$ 's required a trial and error procedure. First, the domains were kept wide and some rough minima was found. The minima was refined by narrowing the domains gradually such that in course of minimisation, the test  $D_{ij}$  values never hit the boundaries.

However, the nature of the function shows that there can be multiple minima. The local minima corresponding to the feasible region was actually found. Thus a widely different set of  $D_{ij}$  values might also minimize the objective function but the  $D_{ij}$  values which were realistic has been found out using this procedure.

#### 4.4 Ternary Diffusivities-Results and Discussion

Ternary diffusivity values were obtained for polystyrene ( $M_w = 32,000$ ) - toluene-cyclohexane mixture at constant polymer concentration ( $w_{PS} = 0.05$ ) but three different toluene and cyclohexane compositions [Table 4.4].

Determination of ternary diffusivities require one of the components to be designated as "solvent" or the "third component". In the present work, there were two choices: first, cyclohexane and second, toluene. Two sets of diffusivities (Results - Sets A and B) were determined considering each of them as the solvent.

It can be seen from Table 4.4 that the deviations from Fick's law are large. The multicomponent effect, i.e., the dominance of the cross terms ( $D_{12}$  and  $D_{21}$ ) over the main terms ( $D_{11}$  and  $D_{22}$ ), was in general stronger than those found by Cussler and Lightfoot [1965a] [Chapter 2] for polystyrene of molecular weight 193,000.

Table 4.4 : Multicomponent diffusivities of polystyrene-toluene-cyclohexane mixture at 28°C

Result-Set A

Components : 1 = Polystyrene ( $M_w = 32000$ )  
 2 = Toluene  
 3 = Cyclohexane

Ternary mixture	1	2	3
$w_1$	0.05	0.05	0.05
$w_2$	0.90	0.70	0.475
$w_3$	0.05	0.25	0.475
$D_{11}$ ( $\text{cm}^2/\text{sec}$ )	$3.032 \times 10^{-6}$	$4.888 \times 10^{-8}$	$3.568 \times 10^{-9}$
$D_{12}$ ( $\text{cm}^2/\text{sec}$ )	$1.184 \times 10^{-6}$	$-2.153 \times 10^{-6}$	$-1.371 \times 10^{-6}$
$D_{21}$ ( $\text{cm}^2/\text{sec}$ )	$4.843 \times 10^{-10}$	$9.992 \times 10^{-7}$	$4.543 \times 10^{-6}$
$D_{22}$ ( $\text{cm}^2/\text{sec}$ )	$1.719 \times 10^{-6}$	$4.685 \times 10^{-6}$	$4.499 \times 10^{-6}$

Continued....

Table 4.4 (continued):Result-Set B

Components : 1 = Polystyrene ( $M_w = 32000$ )

2 = Cyclohexane

3 = Toluene

Ternary mixture	1	2	3
$w_1$	0.05	0.05	0.05
$w_2$	0.05	0.25	0.475
$w_3$	0.90	0.70	0.475
$D_{11}$ ( $\text{cm}^2/\text{sec}$ )	$2.152 \times 10^{-6}$	$1.468 \times 10^{-6}$	$2.347 \times 10^{-8}$
$D_{12}$ ( $\text{cm}^2/\text{sec}$ )	$3.160 \times 10^{-6}$	$7.795 \times 10^{-5}$	$7.544 \times 10^{-6}$
$D_{21}$ ( $\text{cm}^2/\text{sec}$ )	$3.483 \times 10^{-10}$	$8.444 \times 10^{-10}$	$1.987 \times 10^{-6}$
$D_{22}$ ( $\text{cm}^2/\text{sec}$ )	$2.744 \times 10^{-4}$	$1.524 \times 10^{-4}$	$7.766 \times 10^{-6}$

The concentration dependence of the  $D_{ij}$ 's was also stronger compared to those obtained by Cussler and Lightfoot [1965a] . In the data considering cyclohexane as solvent [Results - Set A, Table 4.4 ], among the main terms,  $D_{11}$  showed a large but systematic variation with concentration; whereas  $D_{22}$  remained almost constant. The cross term  $D_{21}$  showed a trend but the variation in  $D_{12}$  was not systematic.

In the data considering toluene as solvent [Results - Set B, Table 4.4 ], there was no discernable variation of the  $D_{ij}$ 's with composition. The  $D_{22}$  values were remarkably larger than the other terms for the first two ternary mixtures. Cussler and Lightfoot [1965a] also reported large  $D_{22}$  values.

The  $D_{ij}$ 's must satisfy the criteria [Cussler and Lightfoot, 1965a ]

$$(D_{11} - D_{22})^2 + 4 D_{12} D_{21} > 0 \quad (4.2)$$

$$D_{11} + D_{22} > 0 \quad (4.3)$$

The first criteria was in-built in the program used to determine the  $D_{ij}$ 's to prevent occurrence of negative quantity under square root. The second criteria was also found to be satisfied with the data.

UNIVERSITY OF TORONTO  
LIBRARY  
87555



In all the experiments, cyclohexane mass fraction was kept the same in the two compartments of the cell and thus there was no driving force for its transfer in the classical sense. Nevertheless, the composition changed in course of the runs, which indicates the non-Fickian behaviour as also seen from the dominance of cross terms as described earlier.

One of the inherent limitation of the present technique is that large composition difference between the upper and the lower compartments is to be maintained. This is necessary to ensure that the change in concentration is much larger than the experimental errors in analysis. However, the diffusivities determined thus may not represent the diffusivity at the arithmetic average of the compositions of the two compartments due to strong non-linear nature of concentration dependence. One way to eliminate this error is to keep the composition differences very small and have very accurate analytical technique. The other is to perform experiments at different composition differences and extrapolate the results to zero composition difference. However, the effort needed is enormous in the later.

The diffusivity data obtained in the present work is not adequate for obtaining a relation for the concentration dependence of ternary diffusivities. Development of a suitable correlation to account for the dependence of

diffusivities on concentration and molecular weight of polymer requires more extensive experimental work.

#### 4.5 Conclusions

The ternary diffusivities of polystyrene-toluene-cyclohexane mixture were determined using the diaphragm cell method. The optimum value of the diffusivity matrix  $[D]$  was determined from the  $\rho_i$  vs.  $t$  data employing a numerical search technique developed by Box. The observed multicomponent effects and the dependence of the diffusivities on composition were stronger than those reported by Cussler and Lightfoot for the same system but differing only in the molecular weight of the polymer. Much more extensive experimental work is needed to obtain the dependence of diffusivities on composition and polymer molecular weight.

# REFERENCES

- Alfrey, T., "Glassy Polymer Diffusion", Chem. Engg. News, 43, No.41, 64 (1965).
- Beveridge, G.S.G., and R.S.Shechter, Optimization : Theory and Practice, McGraw-Hill Kogakusha, Tokyo, Japan (1970).
- Cowie, J.M.C., and E.L.Cussler, "Frictional Behaviour of Polystyrene", J. Chem. Phys., 46, 4886 (1967).
- Crank, J., Mathematics of Diffusion, 2nd Ed., Oxford University Press, London, England (1975).
- Cussler, E.L., Multicomponent Diffusion, Elsevier Scientific Publishing Company, Amsterdam, Netherlands (1976).
- Cussler, E.L., and P.J.Dunlop, "An Experimental Comparison of the Gouy and the Diaphragm Cell Methods for Studying Isothermal Ternary Diffusion", J. Phys. Chem., 70, 1880 (1966).
- Cussler, E.L., and E.N.Lightfoot, "Multicomponent Diffusion Involving High Polymers, I. Diffusion of Monodisperse Polystyrene in Mixed Solvents", J. Phys. Chem., 69, 1135 (1965a).
- Cussler, E.L., and E.N.Lightfoot, "Multicomponent Diffusion Involving High Polymers. III. Ternary Diffusion in the System Polystyrene 1-Polystyrene 2-Toluene", J. Phys. Chem., 69, 2875 (1965b).
- Duda, J.L., and J.S.Vrentas, "Diffusion in Polymer- Solvent Systems. I. Re-examination of the Free-volume Theory", J. Polym. Sci., Polymer Physics Ed., 15, 403 (1977a).
- Duda, J.L., and J.S.Vrentas, "Diffusion in Polymer-Solvent System.II. A Predictive Theory for the Dependence of Diffusion Coefficients on Temperature, Concentration and Molecular Weight", J. Polym. Sci., Polymer Physics Ed., 15, 417 (1977b).
- Duda, J.L., Y.C.Ni and J.S.Vrentas, "Diffusion of Ethylbenzene in Molten Polystyrene", J. Appl. Polymer Sci., 22, 689 (1978).
- Duda, J.L., G.K.Kimmerly, W.L.Sigelko and J.S.Vrentas, Ind. Eng. Chem. Fundam., 12, 133 (1973).

- Dunlop, P.J., B.J.Steel and J.E.Lane, "Experimental Methods for Studying Diffusion in Liquids, Gases and Solids". In A. Weissberger and B.W.Rossiter (Eds.), Physical Methods of Chemistry, Vol.1, Wiley, New York (1972).
- Flory, P.J., and W.R. Krigbaum, "Statistical Mechanics of Dilute Polymer Solutions II", J. Chem. Phys., 18, 1086 (1950).
- Fujita, H., "Organic Vapors Above the Glass Transition Temperature", in Diffusion in Polymers, J. Grank and G.S.Park, ed., Academic Press, New York (1968).
- Fujita, H., and L.J.Gosting, "A New Procedure for Calculating the Four Diffusion Coefficients of Three-Component Systems from Gouy Diffusimeter Data", J. Phys. Chem., 64, 1526 (1960).
- Geankopolis, C.J., M.R.Okos and E.A.Grulke, "Diffusion of Urea and Potassium Chloride in Albumin Solution", J. Chem. Engg. Data, 23, 40 (1978).
- Gordon, A.R., "The Diaphragm Cell Method of Measuring Diffusion", Ann. N.Y.Acad. Sci., 46, 285 (1945).
- Gosting, L.J., E.M.Hanson, G.Kegeles and M.S.Morris, "Equipment and Experimental Methods for Interference Diffusion Studies, Rev. Sci. Instrum., 20, 209 (1949).
- Groot, S.R., and P.Mazur, "Non-Equilibrium Thermodynamics", North Holland Publishing Co., Amsterdam, Netherlands (1962).
- Hopfenberg, H.B., and H.L.Frisch, "Transport of Organic Micromolecules in Amorphous Polymers", J. Polymer Sci., B7, 405 (1969).
- Hughes, R.R. and R.K.Malik, CPX - A General Purpose Program for Constrained Optimisation, in Ph.D. Thesis of R.K. Malik, University of Wisconsin, Madison (1979).
- Kirkwood, J.G., and J.Reisemann, "The Intrinsic Viscosities and Diffusion Constants of Flexible Macromolecules in Solutions", J. Chem. Phys., 16, 565 (1948).

- Mills, R., "The Intradiffusion and Derived Frictional Coefficients for Benzene and Cyclohexane in Their Mixtures at 25°C", J. Phys. Chem., 69, 3116 (1965).
- Mills, R., L.A.Woolf and R.O.Watts, "Simplified Procedures for Diaphragm-cell Diffusion Studies", AIChEJ., 14, 671 (1968).
- Patel, P.R., E.C.Moreno and T.M.Gregory, "Calculation of Diffusion Coefficients in Ternary Systems from Diaphragm-Cell Experiments", Res. Nat. Bur. Stand. Phys. Chem., 73A, 43 (1969).
- Revzin, A., "A New Procedure for Calculating the Four Diffusion Coefficients for Ternary Systems from Gouy Optical Data . Application to Data for the System KBr-HBr-H<sub>2</sub>O at 25°C", J. Phys. Chem., 76, 3419 (1972).
- Robinson, R.A., and R.H.Stokes, Electrolyte Solutions, Butterworths, London (1959).
- Scott, R.L., "Thermodynamics of High Polymer Solutions.V. Phase Equilibria in the Ternary System : Polymer 1-Polymer 2 - Solvent", J. Chem. Phys., 17, 279 (1949).
- Stokes, R.H., "An Improved Diaphragm-Cell for Diffusion Studies, and Some Tests of the Methods", J. Am. Chem. Soc., 72, 763 (1950).
- Stokes, R.H., "Integral Diffusion Coefficients of Potassium Chloride Solutions for Calibration of Diaphragm Cells", J. Am. Chem. Soc., 73, 3527 (1951).
- Toor, H.L., "Diffusion in Three-component Gas Mixture", AIChE J., 3, 198 (1957).
- Toor, H.L., "Solution of the Linearized Equations of Multicomponent Mass Transfer : I", AIChE J., 10, 448 (1964a).
- Toor, H.L., "Solution of the Linearized Equations of Multicomponent Mass Transfer : II Matrix Methods", AIChEJ., 10, 460 (1964b).
- Tsvetkov, V.N., and S.I.Klenin, "A Study of Diffusion in Polymer Solutions by the Use of Polarisation Interferometer", J. Polymer Sci., 30, 187 (1958).

- Vrentas, J.S., and J.L.Duda, "Diffusion in Infinitely Dilute Polystyrene Solutions", J. Appl. Polymer Sci., 20, 1125 (1976a).
- Vrentas, J.S., and J.L.Duda, "Diffusion in Dilute Polystyrene Solutions", J. Polymer Sci., Polymer Phys. Ed., 14, 101 (1976b).
- Vrentas, J.S., and J.L.Duda, "Molecular Diffusion in Polymer Solutions", AIChEJ, 25, No.1 (1979).
- Yamakawa, H., Modern Theory of Polymer Solutions, Harper and Row, New York (1971).

APPENDIX ATable A.1 : Calibration data for toluene-cyclohexane  
binary mixtures at 25°C

$w_T$	$w_{CH}$	Density, $\rho$ (g/ml)
0.00000	1.00000	0.78269
0.20870	0.79130	0.79676
0.43303	0.56697	0.81442
0.63366	0.36634	0.83263
0.81163	0.18837	0.85059
1.00000	0.00000	0.87143

Table A.2 : Calibration data for polystyrene-toluene-cyclohexane ternary mixture at 25°C

Sample No.	w <sub>PS</sub>	w <sub>T</sub>	w <sub>CH</sub>	Density, $\rho$ (g/ml)
1	0.02011	0.00000	0.97989	0.76384
2	0.03971	0.00000	0.96029	0.76790
3	0.05984	0.00000	0.94016	0.77265
4	0.07971	0.00000	0.92029	0.77673
5	0.02364	0.19593	0.78371	0.77684
6	0.04023	0.19195	0.76782	0.78134
7	0.05989	0.18802	0.75208	0.78544
8	0.08159	0.18397	0.73587	0.78959
9	0.01995	0.39202	0.58803	0.79137
10	0.03808	0.38477	0.57715	0.79557
11	0.06016	0.37595	0.56394	0.80023
12	0.08013	0.36795	0.55192	0.80429
13	0.02016	0.58790	0.39193	0.80904
14	0.03996	0.57602	0.38401	0.81349
15	0.06000	0.56399	0.37599	0.81712
16	0.08019	0.55188	0.36792	0.82121
17	0.01989	0.78408	0.19602	0.82867
18	0.03986	0.76811	0.19203	0.83207
19	0.06012	0.75191	0.18798	0.83614
20	0.07998	0.73602	0.18400	0.84023
21	0.02025	0.97974	0.00000	0.84960
22	0.03994	0.96006	0.00000	0.86312
23	0.06003	0.93997	0.00000	0.85699
24	0.07978	0.92022	0.00000	0.86030
25	0.09007	0.90993	0.00000	0.86429
26	0.01491	0.98508	0.00000	0.85166



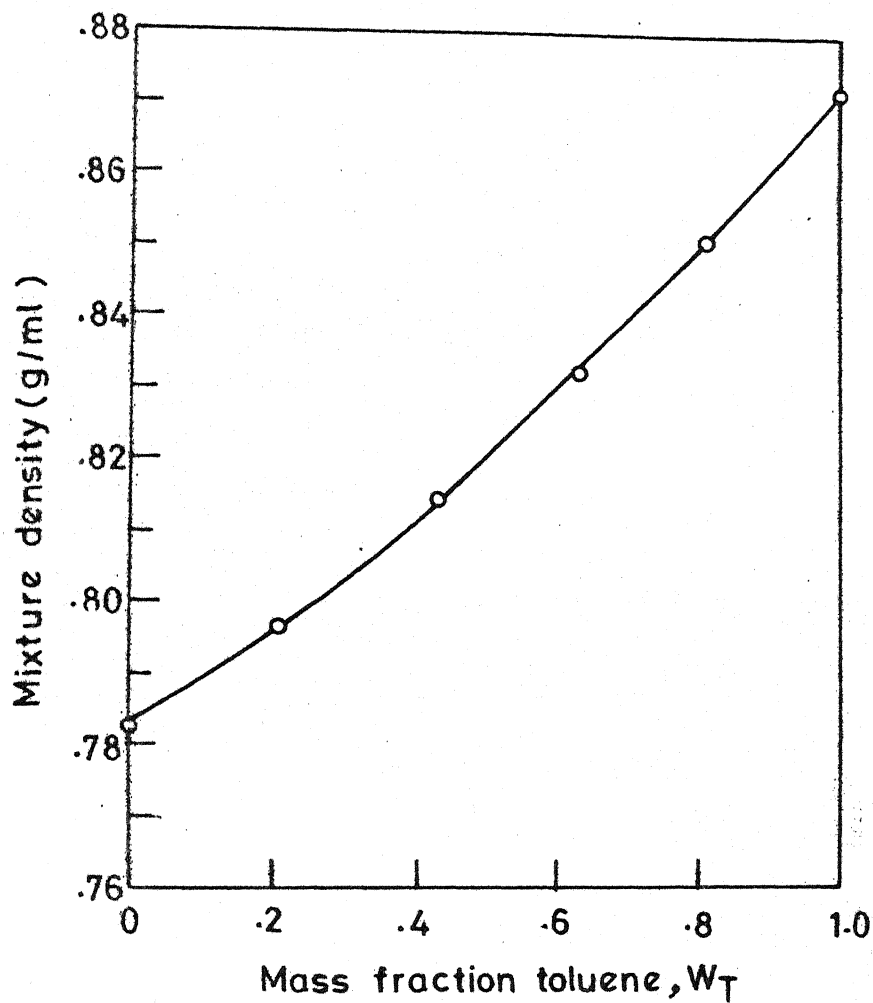


FIG. A.1 CALIBRATION CURVE FOR TOLUENE-CYCLOHEXANE  
BINARY MIXTURE AT 25°C [Ref. Table A.1]

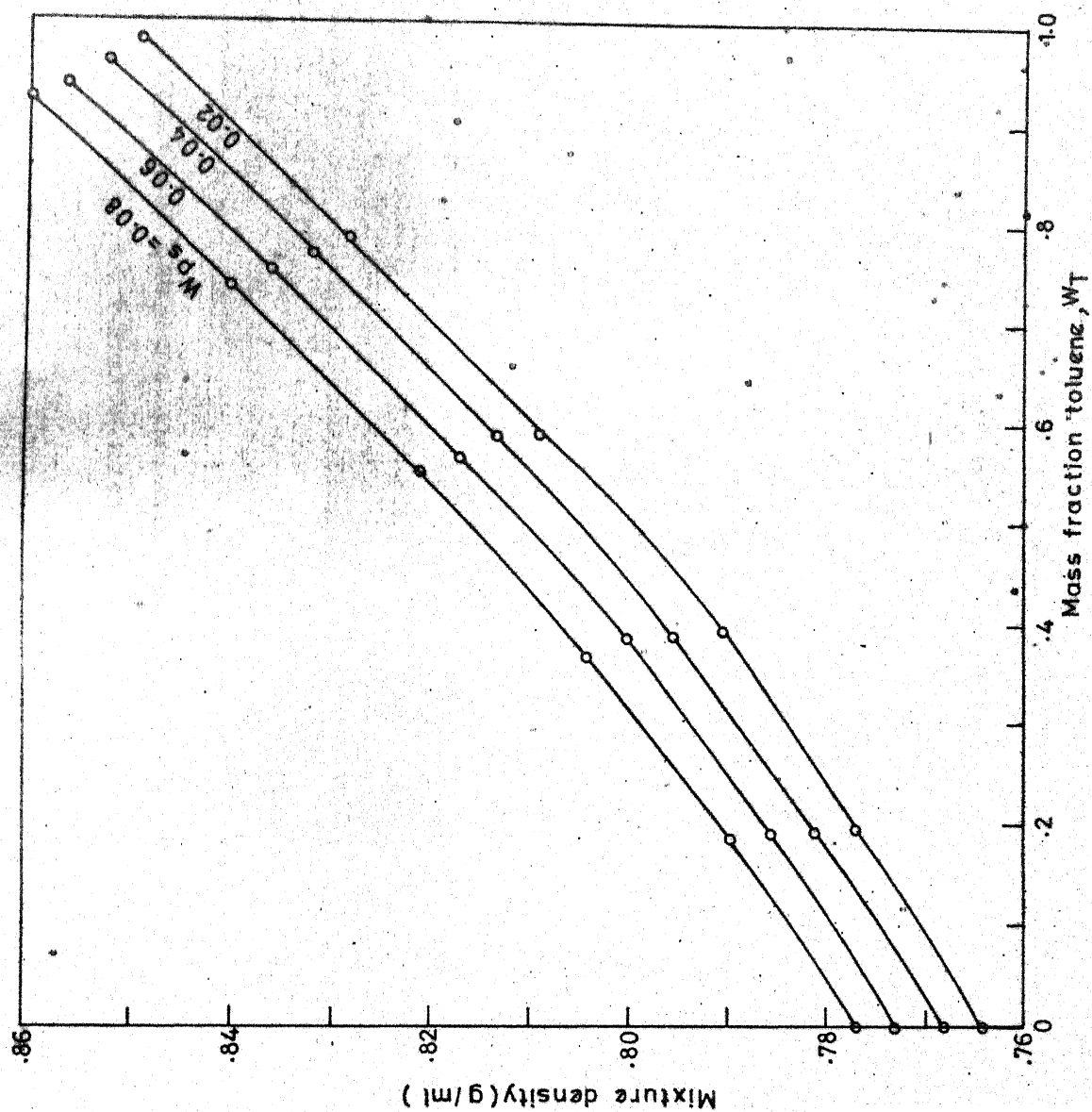


FIG. A.2 CALIBRATION CURVE FOR POLYSTYRENE-TOLUENE-CYCLOHEXANE  
TERNARY MIXTURE AT 25°C. [Ref. Table A.2]

## APPENDIX B

Table B.1 : Binary data for toluene-cyclohexane mixture at 25°C

Note : The following data were used for cell constant determination

	Time (hr)	Compartment L = lower U = upper	Density, $\rho$ (g/ml)	$w_T$	$\rho_T = w_T x \rho$ (g/ml)	$\Delta \rho_T = (\rho_L - \rho_U)$ (g/ml)
Diaphragm 1	0	L	0.82862	0.59537	0.49334	
	0	U	0.81800	0.47811	0.39109	0.10225
	0.5	L	0.82689	0.57688	0.47702	
	0.5	U	0.81995	0.50035	0.41026	0.06675
	1.0	L	0.82529	0.55959	0.46182	
	1.0	U	0.82085	0.51051	0.41905	0.04277
	1.5	L	0.82453	0.55130	0.45456	
	1.5	U	0.82162	0.51914	0.42653	0.02803
Diaphragm 2	0	L	0.82563	0.56328	0.46506	
	0	U	0.81515	0.44498	0.36273	0.10233
	0.5	L	0.82436	0.54382	0.44830	
	0.5	U	0.81715	0.48631	0.38268	0.06562
	1.0	L	0.82270	0.53115	0.43698	
	1.0	U	0.81821	0.48053	0.39317	0.04381
	1.5	L	0.82186	0.52182	0.42886	
	1.5	U	0.81899	0.48945	0.40086	0.02800

Table B.2 : Binary data for benzene-cyclohexane mixture  
at 28°C

Time (hr)	Compartment L = lower U = upper	Density, $\rho$ (g/ml)	$\Delta \rho = \rho_U - \rho_L$ (g/ml)
0	L	0.86512	
0	U	0.85016	0.01496
0.5	L	0.86245	
0.5	U	0.85274	0.00971
1.0	L	0.86060	
1.0	U	0.85487	0.00573
1.5	L	0.85973	
1.5	U	0.85567	0.00406

Table B.3 : Binary data for polystyrene-toluene mixture at 28°C

Time (hr)	Compartment L = lower U = upper	Density, $\rho$ (g/ml)	$w_{PS}$	$\rho_{PS} = w_{PS}$ (g/ml)	$\Delta \rho_{PS} = (\rho_U \sim \rho_L)_{PS}$ (g/ml)
0	L	0.84862	0.01971	0.01672	
0	U	0.85923	0.07819	0.06718	0.05046
7	L	0.85089	0.03101	0.02638	
7	U	0.85761	0.06771	0.05807	0.03169

Table B.4 : Ternary raw data (Set 1) for polystyrene-toluene-cyclohexane mixture at 25°C

[Ref.: Fig.B.4]

Set 1

Composition :  $w_{PS} = 0.05$

$w_T = 0.90$

$w_{CH} = 0.05$

Time (hr)	Compartment L = lower U = upper	Density, $\rho$ (g/ml)	$w_{PS}$
0.00	L	0.85477	0.07982
0.00	U	0.84369	0.02002
2.00	L	0.85351	0.07556
2.00	U	0.84490	0.02606
3.25	L	0.85272	0.07180
3.25	U	0.84502	0.02882
4.50	L	0.85297	0.07223
4.50	U	0.84540	0.02963
5.75	L	0.85268	0.06892
5.75	U	0.84581	0.03326

Table B.5 : Ternary raw data (Set 2) for polystyrene-toluene-cyclohexane mixture at 25°C

[Ref. : Fig. B.5]

Set 2

Composition :  $w_{PS} = 0.05$   
 $w_T = 0.70$   
 $w_{CH} = 0.25$

Time (hr)	Compartment L = lower U = upper	Density, $\rho$ (g/ml)	$w_{PS}$
0	L	0.83314	0.07932
0	U	0.82297	0.01917
1	L	0.83299	0.07699
1	U	0.82309	0.02194
2	L	0.83276	0.07560
2	U	0.82289	0.02360
3	L	0.83268	0.07323
3	U	0.82356	0.02536
4	L	0.83221	0.07319
4	U	0.82394	0.02685
5	L	0.83218	0.07094
5	U	0.82391	0.02847

Table B.6 : Ternary raw data (Set 3) for polystyrene-toluene-cyclohexane mixture at 25°C

[Ref.: Fig.B.6 ]

Set 3

Composition :  $w_{PS} = 0.05$   
 $w_T = 0.475$   
 $w_{CH} = 0.475$

Time (hr)	Compartment L = lower U = upper	Density, $\rho$ (g/ml)	$w_{PS}$
0	L	0.81119	0.07897
0	U	0.80142	0.01960
1	L	0.81093	0.07837
1	U	0.80180	0.02192
2	L	0.81019	0.07635
2	U	0.80221	0.02397
3	L	0.81031	0.07465
3	U	0.80224	0.02518
4	L	0.80960	0.07282
4	U	0.80329	0.02678
5	L	0.80937	0.07250
5	U	0.80334	0.02811



Table B.7 : Smoothed ternary data (Set 1) for polystyrene-toluene-cyclohexane mixture at 25°C

Note: The following data are read from graphs in Fig.B.4

Set 1

Composition:  $w_{PS} = 0.05$   
 $w_T = 0.90$   
 $w_{CH} = 0.05$

Time (hr)	Compartment L = lower U = upper	Density, $\rho$ (g/ml)	$w_{PS}$	$w_T$	$w_{CH}$
0	L	0.85477	0.07982	0.86957	0.05061
0	U	0.84369	0.02002	0.92458	0.05540
2.00	L	0.85351	0.07461	0.87106	0.05433
2.00	U	0.84467	0.02606	0.91921	0.05473
3.25	L	0.85303	0.07250	0.87210	0.05540
3.25	U	0.84520	0.02882	0.91726	0.05392
4.50	L	0.85276	0.07070	0.87429	0.05501
4.50	U	0.84559	0.03130	0.91459	0.05411
5.75	L	0.85268	0.06959	0.87645	0.05395
5.75	U	0.84581	0.03510	0.90683	0.05807

**Table B.8 :** Smoothened ternary data (Set 2) for polystyrene-toluene-cyclohexane mixture at 25°C.

Note: The following data are read from graphs in Fig.B.5

**Set 2**

Composition :  $w_{PS} = 0.05$

$w_T = 0.70$

$w_{CH} = 0.25$

Time (hr)	Compartment L = lower U = upper	Density, $\rho$ (g/ml)	$w_{PS}$	$w_T$	$w_{CH}$
0	L	0.83314	0.07932	0.67132	0.24936
0	U	0.82297	0.01918	0.73130	0.24952
1	L	0.83299	0.07699	0.67619	0.24682
1	U	0.82321	0.02194	0.72634	0.25172
2	L	0.83272	0.07500	0.67901	0.24599
2	U	0.82343	0.02500	0.72414	0.25226
3	L	0.83248	0.07323	0.68152	0.24525
3	U	0.82362	0.02536	0.72139	0.25325
4	L	0.83233	0.07183	0.68386	0.24430
4	U	0.82389	0.02685	0.72018	0.25298
5	L	0.83222	0.07094	0.68522	0.24384
5	U	0.82410	0.02847	0.71802	0.25351

Table B.9 : Smoothed ternary data (Set 3) for polystyrene-toluene-cyclohexane mixture at 25°C

Note: The following data are read from graphs in Fig.B.6

Set 3

Composition :  $w_{PS} = 0.05$

$w_T = 0.475$

$w_{CH} = 0.475$

Time (hr)	Compartment L = lower U = upper	Density, $\rho$ (g/ml)	$w_{PS}$	$w_T$	$w_{CH}$
0	L	0.81119	0.07897	0.44946	0.47158
0	U	0.80142	0.01960	0.50848	0.47192
1	L	0.81061	0.07700	0.44868	0.47431
1	U	0.80180	0.02192	0.50501	0.47307
2	L	0.81022	0.07540	0.44890	0.47570
2	U	0.80221	0.02397	0.50291	0.47312
3	L	0.80989	0.07440	0.44806	0.47754
3	U	0.80267	0.02530	0.50382	0.47088
4	L	0.80960	0.07281	0.44927	0.47792
4	U	0.80304	0.02690	0.50294	0.47016
5	L	0.80937	0.07250	0.44759	0.47991
5	U	0.80334	0.02811	0.50255	0.46934

Table B.10 : Ternary  $\rho_i$  vs.  $t$  data (Set 1) for polystyrene-toluene-cyclohexane mixture at 25°C

Note : The following data were calculated using Table B.7

Set 1

Composition :  $w_{PS} = 0.05$   
 $w_T = 0.90$   
 $w_{CH} = 0.05$

Time (sec.)	Compartment L= lower U= upper	$\rho_{PS}$ (g/ml)	$\rho_T$ (g/ml)	$\rho_{CH}$ (g/ml)	$\Delta \rho_{PS}$ (g/ml)	$\Delta \rho_T$ (g/ml)	$\Delta \rho_{CH}$ (g/ml)
0	L	0.0682300	0.7432829	0.0432571			
0	U	0.0168913	0.7800598	0.0467388	0.0513386	-0.0367769	-0.0034817
7200	L	0.0636806	0.7434584	0.0463709			
7200	U	0.0220536	0.7764308	0.0462312	0.0416726	-0.0329724	0.0001398
11700	L	0.0618448	0.7439242	0.0472610			
11700	U	0.0243578	0.7752687	0.0455734	0.0374869	-0.0313445	0.0016876
16200	L	0.0602938	0.7455569	0.0469093			
16200	U	0.0264665	0.7733699	0.0457535	0.0338273	-0.0278130	0.0011558
20700	L	0.0593389	0.7473353	0.0460058			
20700	U	0.0296901	0.7670053	0.0491146	0.0296487	-0.0196700	-0.0031087

Table B.11 : Ternary  $\rho_i$  vs.  $t$  data (Set 2) for polystyrene-toluene-cyclohexane mixture at 25°C.

Note : The following data were calculated using Table B.8

Set 2

Composition:  $w_{PS} = 0.05$   
 $w_T = 0.70$   
 $w_{CH} = 0.25$

Time (sec.)	Compartment L = lower U = upper	$\rho_{PS}$ (g/ml)	$\rho_{T_i}$ (g/ml)	$\rho_{CH}$ (g/ml)	$\Delta\rho_{PS}$ (g/ml)	$\Delta\rho_T$ (g/ml)	$\Delta\rho_{CH}$ (g/ml)
0	L	0.0660867	0.5593053	0.2077480			
0	U	0.0157811	0.6018415	0.2053474	0.0503056	-0.0425362	0.0024006
3600	L	0.0641322	0.5632619	0.2055958			
3600	U	0.0180640	0.5979267	0.2072192	0.0460682	-0.0346648	-0.0016234
7200	L	0.0624538	0.5654237	0.2048425			
7200	U	0.0194322	0.5962775	0.2077203	0.0430216	-0.0308537	-0.0028779
10800	L	0.0609591	0.5673555	0.2041654			
10800	U	0.0208905	0.5941484	0.2085812	0.0400686	-0.0267928	-0.0044158
14400	L	0.0597898	0.5691984	0.2033419			
14400	U	0.0221181	0.5933454	0.2084265	0.0376717	-0.0241470	-0.0050847
18000	L	0.0590417	0.5702535	0.2029249			
18000	U	0.0234611	0.5917241	0.2089148	0.0355805	-0.0214706	-0.0059899

Table B.12 : Ternary  $\rho_i$  vs.  $t$  data (Set 3) for polystyrene-toluene-cyclohexane mixture at 25°C

Note : The following data were calculated using Table B.9

Set 3

Composition:  $w_{PS} = 0.05$   
 $w_T = 0.475$   
 $w_{CH} = 0.475$

Time (sec)	Compartment L = lower U = upper	$\rho_{PS}$ (g/ml)	$\rho_T$ (g/ml)	$\rho_{CH}$ (g/ml)	$\Delta\rho_{PS}$ (g/ml)	$\Delta\rho_T$ (g/ml)	$\Delta\rho_{CH}$ (g/ml)
0	L	0.0640576	0.3645939	0.3825385			
0	U	0.0157084	0.4075030	0.3782086	0.0483493	-0.0429091	0.0043299
3600	L	0.0624179	0.3637080	0.3844842			
3600	U	0.0175714	0.4049210	0.3793075	0.0448464	-0.0412130	0.0051766
7200	L	0.0610923	0.3637057	0.3854221			
7200	U	0.0192320	0.4034398	0.3795382	0.0418603	-0.0397341	0.0058838
10800	L	0.0602546	0.3628819	0.3867535			
10800	U	0.0203085	0.4044004	0.3779611	0.0399461	-0.0415185	0.0087924
14400	L	0.0589480	0.3637317	0.3869203			
14400	U	0.0216038	0.4038773	0.3775589	0.0373442	-0.0401457	0.0093614
18000	L	0.0586783	0.3622636	0.3884281			
18000	U	0.0225840	0.4037204	0.3770357	0.0360943	-0.0414567	0.0113924

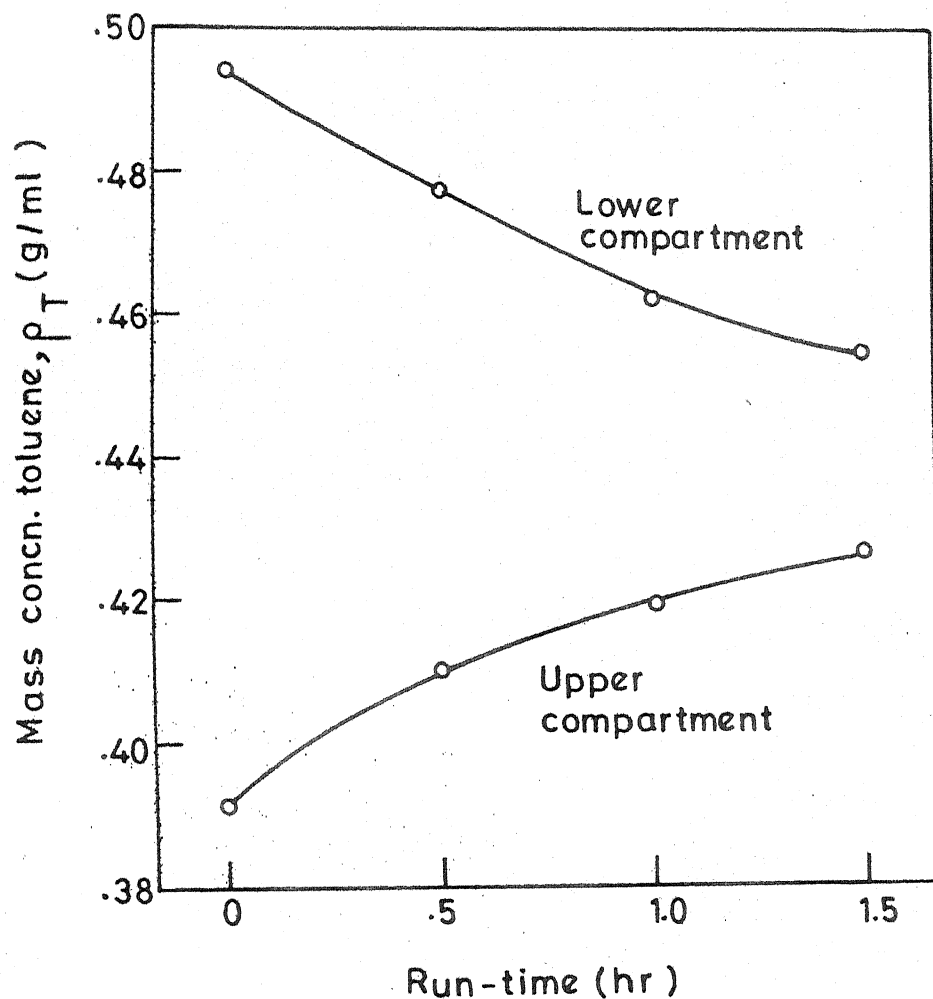


FIG. B.1 BINARY DATA FOR TOLUENE - CYCLOHEXANE MIXTURE AT 28°C FOR DIAPHRAGM 1 [Ref.: Table B.1]

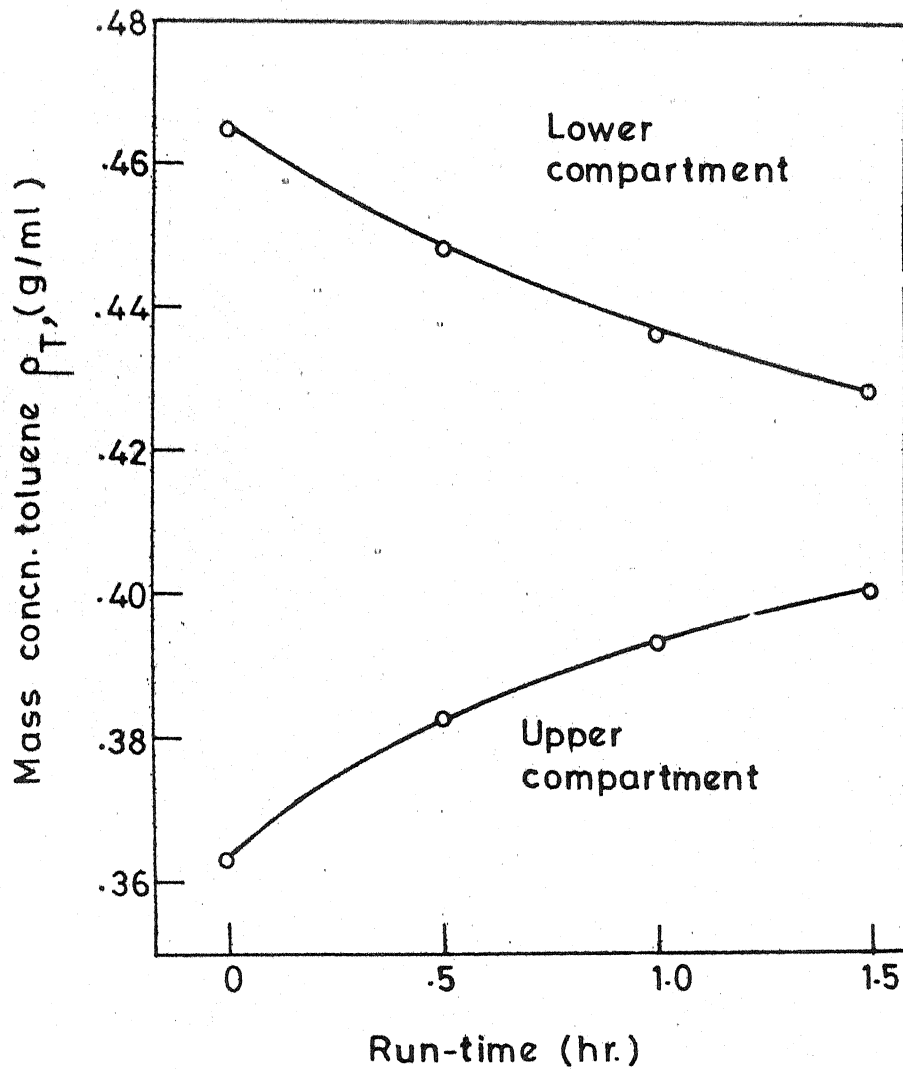


FIG B.2 BINARY DATA FOR TOLUENE - CYCLOHEXANE MIXTURE AT 28°C FOR DIAPHRAGM 2 .  
[Ref.: Table B.1]



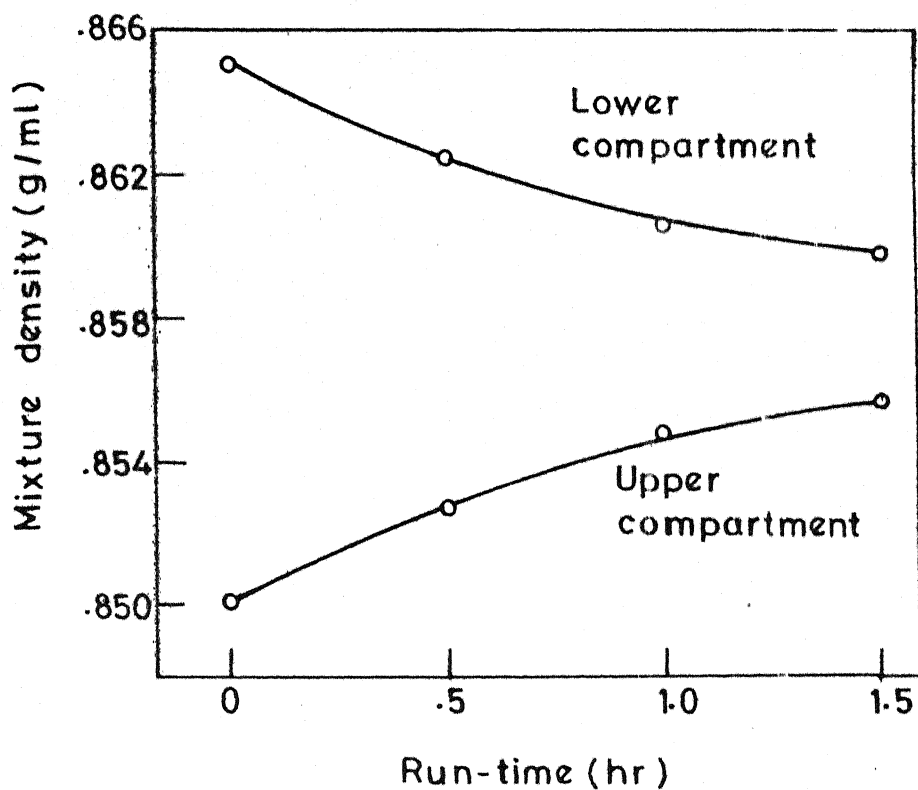


FIG B.3 BINARY DATA FOR BENZENE - CYCLOHEXANE MIXTURE AT 28°C [Ref.: Table B.2]

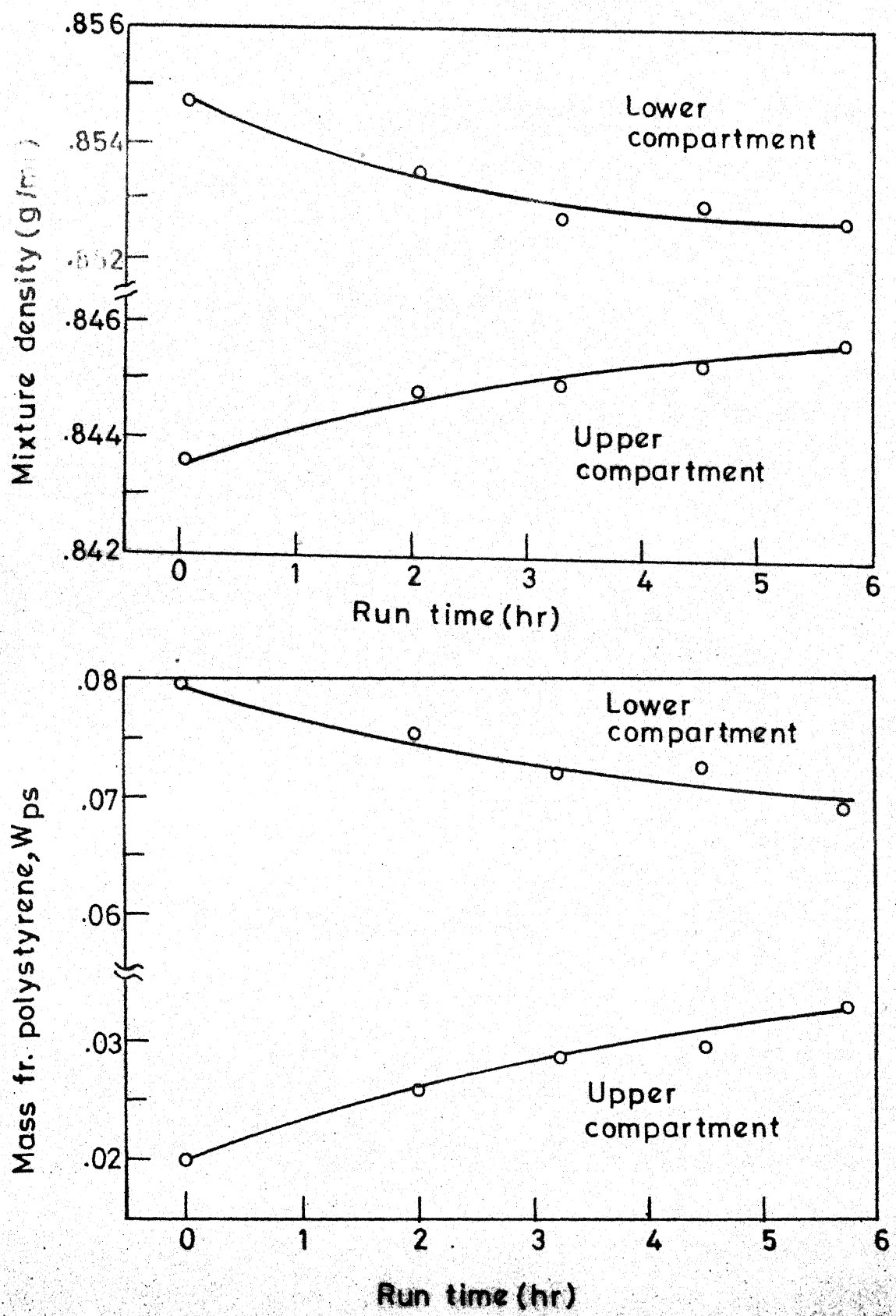


FIG. B.4 TERNARY DATA FOR POLYSTYRENE-TOLUENE-CYCLOHEXANE MIXTURE (SET 1) AT 25°C  
[Ref.: Table B.4]

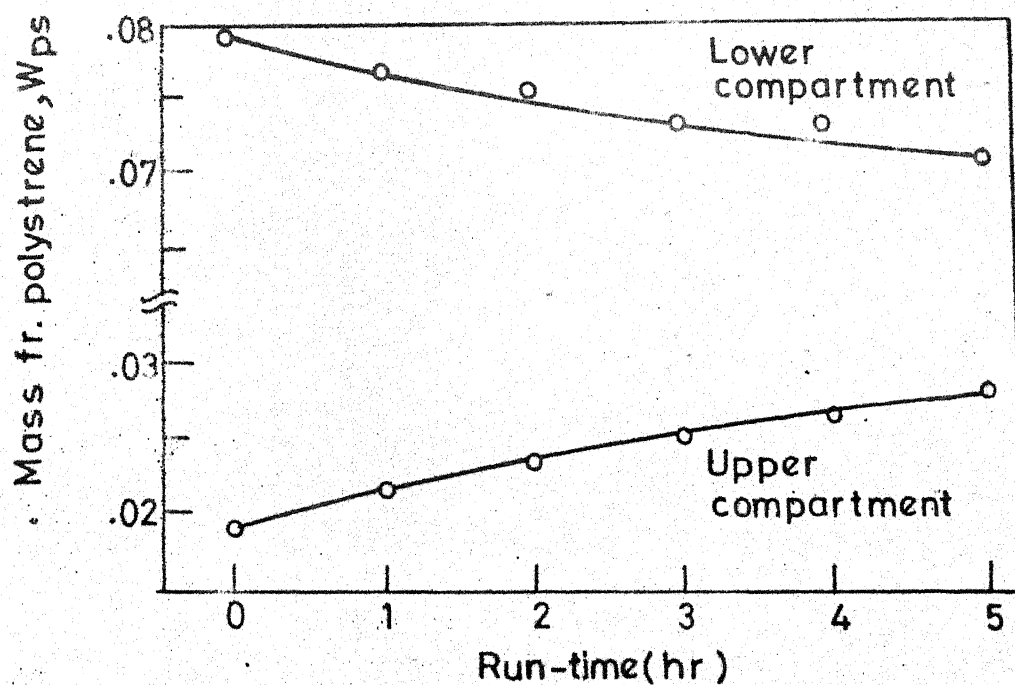
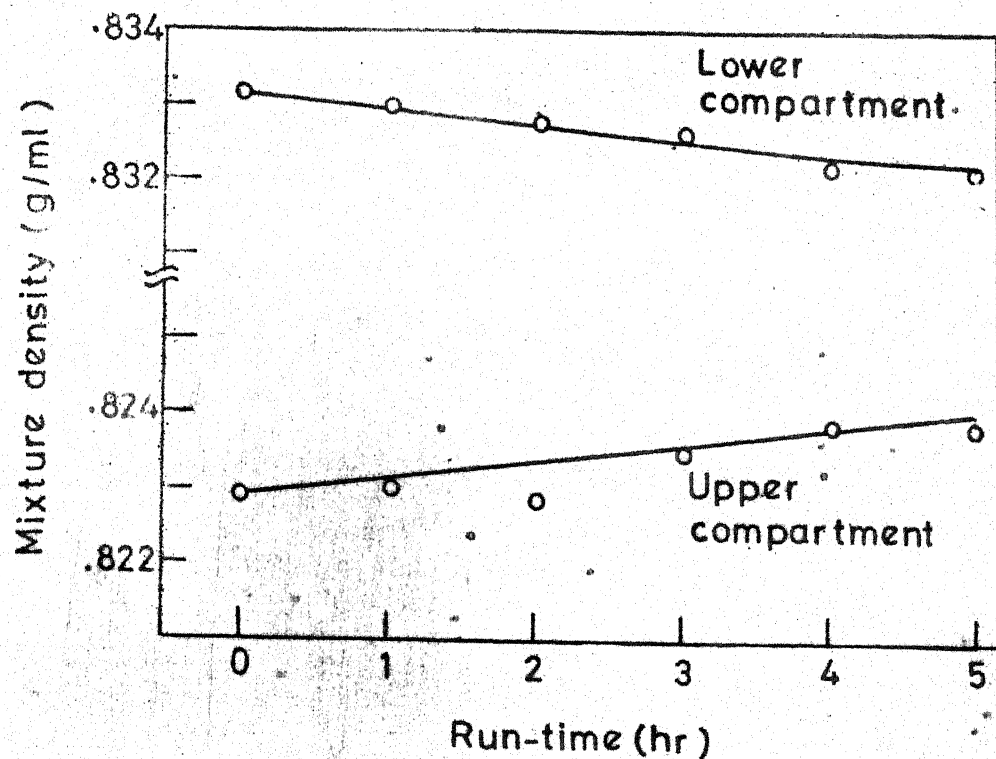


FIG. B.5 TERNARY DATA FOR POLYSTYRENE-TOLUENE  
-CYCLOHEXANE MIXTURE (SET 2) AT 25°C  
[Ref.: Table B.5]

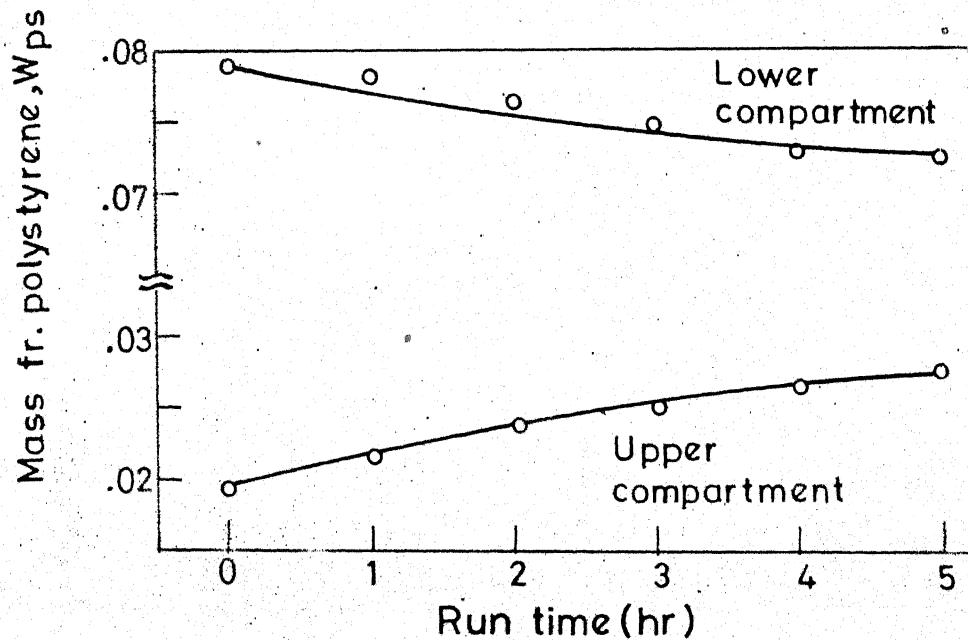
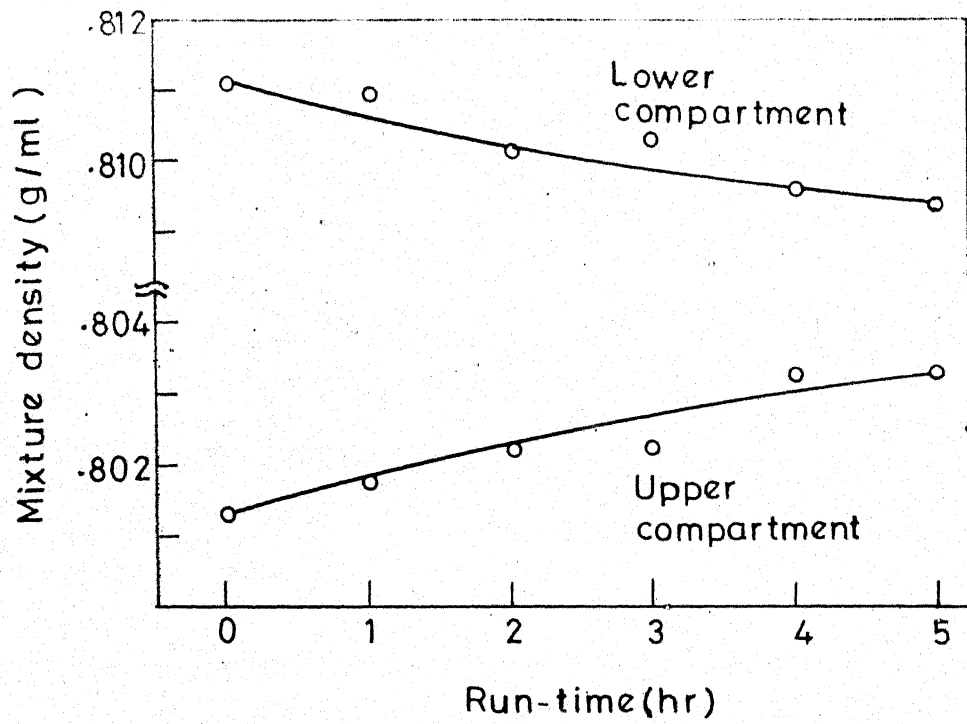


FIG. B.6 TERNARY DATA FOR POLYSTYRENE - TOLUENE - CYCLOHEXANE MIXTURE (SET 3) AT 25°C  
[Ref.: Table B.6]